

A meta substitution leaves the moment unchanged in magnitude.

An ortho substitution increases the moment and therefore increases the specific inductive capacity.

It would seem that determinations of the specific inductive capacity might be useful in determining whether the second substituent went into the para, ortho, or meta position.

If the second substituent is not the same as the first, thus if I' is the moment due to the second, the moment of the molecule if the second substituent goes into :

- (1) The para position is $I - I'$.
- (2) The ortho position is $(I^2 + I'^2 + II')^{1/2}$.
- (3) The meta position is $(I^2 + I'^2 - II')^{1/2}$.

If I and I' have the same sign, *i.e.*, if both substituents belong to the same type, the specific inductive capacity will be least for the para position and greatest for the ortho—that for the meta position will be between the values for the para and ortho.

If, however, the two substituents belong to different types I' will be of the opposite sign to I , and the specific inductive capacity will be *greatest* in the para position and least in the ortho.

LV. On a Second Approximation to the Quantum Theory of the Simple Zeeman Effect and the Appearance of New Components. By A. M. MOSHARRAFA, King's College, London..*

§ 1. *The Hypothetical Path of Equal Energy.*

IN a previous paper † a first approximation to the theory of the simple Zeeman effect was put forward, based on the extended form of the quantum restrictions, viz.

$$\int_0 (p_i - ea_i) dq_i = n_i h, \quad i = 1, 2, 3, \dots, \dots \quad (1)$$

where a is the magnetic vector potential and the integration extends from $q_i = \text{minimum}$ to $q_i = \text{maximum}$ and back again. It was found that the method of separation of the variables could be successfully applied in the presence of the field H , provided all terms of higher order than the first in H were

* Communicated by Prof. O. W. Richardson, F.R.S.

† Roy. Soc. Proc. A, vol. cii. p. 529 (1923). This will be referred to freely.

neglected. In this paper we shall show that the method can still be applied, without any restriction as to the degree of approximation, to a hypothetical motion which possesses the same energy as the actual motion.

Let Σ^* be one of the actual paths of the electron in the presence of the field. Thus Σ is completely defined by the following six equations in spherical polar coordinates† with the origin in the nucleus and Oz in the direction of H :

$$\left. \begin{aligned} d(m\dot{r})/dt - mr\dot{\theta}^2 - mr\sin^2\theta\dot{\psi}^2 &= -eE/r + K_r, \quad (\alpha) \\ \frac{1}{r}d(mr^2\dot{\theta})/dt - mr\sin\theta\cos\theta\dot{\psi}^2 &= K_\theta, \quad \dots \quad (\beta) \\ \frac{1}{r\sin\theta}d(mr^2\sin^2\theta\dot{\psi})/dt &= K_\psi, \quad \dots \quad (\gamma) \end{aligned} \right\} \quad (2)$$

$$\left. \begin{aligned} \int_0^r p_r dr &= n_1 h, \quad \dots \quad (\alpha) \\ \int_0^\theta p_\theta d\theta &= n_2 h, \quad \dots \quad (\beta) \\ \int_0^\psi (p_\psi - m_0\omega r^2 \sin^2\theta) d\psi &= n_3 h, \quad \dots \quad (\gamma) \end{aligned} \right\} \quad (3)$$

where m is the mass of the electron [variable], m_0 is the value of m for zero velocity, $(-e)$ and E are the charges on the electron and nucleus respectively, ω is given by

$$\omega = eH/2m_0c, \quad \dots \quad (4)$$

and K is the so-called "Coriolis" force acting on the electron on account of its motion in the magnetic field, being equal per unit charge to the vector product of the velocity and the field. Thus

$$\left. \begin{aligned} K_r &= -eHr\sin^2\theta\dot{\psi}/c, \quad \dots \quad (\alpha) \\ K_\theta &= -eHr\sin\theta\cos\theta\dot{\psi}/c, \quad \dots \quad (\beta) \\ K_\psi &= eH(\dot{r}\sin\theta + r\cos\theta\dot{\theta})/c. \quad (\gamma) \end{aligned} \right\} \quad (5)$$

Consider a hypothetical path Γ defined by the six equations obtained from (2) and (3) by putting $K_r = K_\theta = K_\psi = 0$ in the former but without altering the latter in any way. Σ can thus be conceived to be derived from Γ by the operation of

* Σ and Γ here used to denote the complete specific motions in the two respective cases.

† The proof is equally valid for any set of coordinates. We choose spherical polars in this section merely because they are adopted in the rest of the paper.

the coriolic forces alone *. Now the element of work done by the coriolic forces is equal to

$$(K_r v_r + K_\theta v_\theta + K_\psi v_\psi) dt,$$

where v is the velocity of the electron at the time considered. And, on using the values of v_r , v_θ , and v_ψ in terms of the coordinates, viz.

$$v_r = \dot{r}, \quad v_\theta = r\dot{\theta}, \quad v_\psi = r \sin \theta \dot{\psi},$$

this is seen from (5) to be identically equal to 0. In other words, the introduction of the coriolic forces alone cannot affect the energy of the electron, and therefore

$$W(\Sigma) = W(\Gamma) = W, \text{ say,} \quad (6)$$

where $W(\Sigma)$ and $W(\Gamma)$ are the respective energies of the two paths. Hence we may calculate the value of W by considering the motion in Γ instead of in Σ .

§ 2. The Expression for W .

Any path Γ is a "relativity ellipse," the dimensions of which are defined by the modified quantum restrictions (3). We thus have for Γ , from the analysis given in § 2 of our previous paper, on putting $H=0$:

$$\left. \begin{aligned} p_r &= m\dot{r} = \sqrt{[A + 2B/r + C/r^2]}, & (\alpha) \\ p_\theta &= mr^2\dot{\theta} = \sqrt{[p^2 - F^2/\sin^2 \theta]}, & (\beta) \\ p_\psi &= mr^2 \sin^2 \theta \dot{\psi} = F, & (\gamma) \end{aligned} \right\} \quad (7)$$

where A , B , and C are given by

$$\left. \begin{aligned} A &= 2m_0W(1 + W/2m_0c^2), & (\alpha) \\ B &= eEm_0(1 + W/m_0c^2), & (\beta) \\ C &= -(p^2 - e^2E^2/c^2), & (\gamma) \end{aligned} \right\} \quad (8)$$

and p and F are constants. From (3) and (7) we have

$$\left. \begin{aligned} \int_0^\infty \sqrt{[A + 2B/r + C/r^2]} dr &= n_1 h, & (\alpha) \\ \int_0^\pi \sqrt{[p^2 - F^2/\sin^2 \theta]} d\theta &= n_2 h, & (\beta) \\ \int_0^{2\pi} [F - m_0\omega r^2 \sin^2 \theta] d\psi &= n_3 h, & (\gamma) \end{aligned} \right\} \quad (9)$$

* It must be clearly understood that this cannot be achieved by actually introducing the magnetic field, since the introduction of a magnetic field involves other forces besides K , viz. the induction forces, which do in fact alter the energy.

and the first two integrals yield as before

$$\begin{aligned} 2\pi i[\sqrt{C} + B/\sqrt{A}] &= n_1 h, \dots \quad (\alpha) \\ 2\pi(p - F) &= n_2 h. \dots \quad (\beta) \end{aligned} \quad (10)$$

To evaluate the third integral we have to deal with

$$I = \omega m_0 \int_0^{2\pi} r^2 \sin^2 \theta d\psi, \dots \quad (11)$$

or since

$$m = m_0/\sqrt{(1-\beta^2)}, \dots \quad (12)$$

we have from (7γ), (11), and (12),

$$I = \omega F \int_0^T \sqrt{(1-\beta^2)} dt, \dots \quad (13)$$

where T is the time from $\psi=0$ to $\psi=2\pi$. Let

$$T = T_0 + \delta_\omega T + \delta_\alpha T + \dots, \dots \quad (14)$$

where $\delta_\omega T$ and $\delta_\alpha T$ are first-order terms in ω and α respectively, α being given by

$$\alpha = (2\pi)^2 e^2 E^2 / h^2 c^2, \dots \quad (15)$$

and T_0 being the value of T calculated for $\omega=\alpha=0$.

We have as a first approximation to the value of I :

$$I = \omega F T_0 + \dots, \dots \quad (16)$$

where $T_0 = (n_1 + n)^3 / 2N, \dots \quad (17)$

N being the Rydberg constant

$$N = (2\pi)^2 m_0 e^2 E^2 / 2h^3 \dots \quad (18)$$

and

$$n = n_2 + n_3. \dots \quad (19)$$

From (9γ), (11), and (16), we have

$$2\pi F = n_3 h [1 + \omega T_0 / 2\pi + \dots]. \dots \quad (10\gamma)$$

Thus, as a first approximation, the motion in Γ is defined by exactly the same equations as in the ordinary Bohr-Sommerfeld atom, except that n_3 is now replaced by

$$n_3(1 + \omega T_0 / 2\pi).$$

Hence, using (17),

$$T_0 + \delta_\omega T = [n_1 + n_2 + n_3(1 + \omega T_0 / 2\pi)]^3 / 2N$$

to the first order,

so that $\delta_\omega T / T_0 = 3n_3 \omega T_0 / 2\pi(n + n_1). \dots \quad (20)$

Now I can be put in the form

$$I = \omega F(1 + \delta_\omega T/T_0) \int_0^{T_0 + \delta_\omega T} \sqrt{(1 - \beta^2)} dt . . . (21)$$

to the second order, where the last integral is evaluated for $\omega=0$. This evaluation is quite independent of a magnetic field, and merely relates to the Bohr-Sommerfeld atom. Quoting here the result given in the Appendix (*q.v.*) for this integral, and using the value for F given by (10 γ), we have

$$I = n_3 h \{ 1 + f_1(n) \cdot \omega T_0 / 2\pi - \alpha f_2(n) \} \omega T_0 / 2\pi, \quad (22)$$

where

$$\left. \begin{aligned} f_1(n) &= 1 + 3n_3/(n+n_1), & \dots & \dots & \dots & \dots & \text{(\alpha)} \\ f_2(n) &= [1 + 5n_1/2n + n_1^2/2n^2]/(n_1+n)^2. & (\beta) \end{aligned} \right\} \quad (23)$$

Equations (9 γ), (11), and (22) finally yield

$$2\pi F = n_3 h \{ 1 + \omega T_0 / 2\pi + f_1(n) (\omega T_0 / 2\pi)^2 - f_2(n) \cdot \alpha \omega T_0 / 2\pi + \dots \}. \quad (10 \gamma a)$$

Thus the equations defining Γ are identical, to the second order of small quantities, with those defining the normal atom if we write n_3' for n_3 , where

$$n_3' = n_3 \{ 1 + \omega T_0 / 2\pi + f_1(n) \cdot (\omega T_0 / 2\pi)^2 - f_2(n) \cdot \alpha \omega T_0 / 2\pi \}. \quad (24)$$

The change in energy can thus at once be calculated from the normal expression for the energy by making this substitution. The normal expression for the energy can be put in the form

$$W_{\text{norm.}} = -Nh \{ 1 + \alpha \phi_1(n_1/n)/(n_1+n)^2 + \alpha^2 \phi_2(n_1/n)/(n_1+n)^4 + \dots \} / (n_1+n)^2, \quad (25)$$

where

$$\left. \begin{aligned} \phi_1(n_1/n) &= 1/4 + n_1/n, & \dots & \dots & \dots & \dots & \text{(\alpha)} \\ \phi_2(n_1/n) &= 1/8 + 3n_1/4n + 3n_1^2/2n^2 + n_1^3/4n^3; & (\beta) \end{aligned} \right\} \quad (26)$$

from which we calculate, using (23), (26 α), and (17) :

$$\left. \begin{aligned} \delta_\omega W &= n_3 h \omega / 2\pi, & \dots & \dots & \dots & \dots & \text{(\alpha)} \\ \delta_\alpha W &= -Nh \alpha \phi_1(n_1/n) / (n_1+n)^4, & \dots & \dots & \dots & \dots & \text{(\beta)} \\ \delta_{\omega^2} W &= (n_1+n)^3 n_3 h \omega^2 [1 + 3n_3/2(n_1+n)] / 2 \cdot (2\pi)^2 N, & (\gamma) \\ \delta_{\alpha^2} W &= -Nh \alpha^2 \phi_2(n_1/n) / (n_1+n)^6, & \dots & \dots & \dots & \dots & \text{(\delta)} \\ \delta_{\omega, \alpha} W &= -n_3 \omega \alpha h / 4\pi (n+n_1)^2. & \dots & \dots & \dots & \dots & \text{(\epsilon)} \end{aligned} \right\} \quad (27)$$

§ 3. Significance of the Results of § 2, and General Character of the Zeeman Decomposition.

Of the five increments of energy given by (27) the first two merely give the simple Zeeman triplet and the first-order fine structure respectively, as already dealt with in the last paper. (27 δ) is the second-order term for the fine structure and leads to a change in wave-length of the order 10^{-5} Å, which is much too small to be detected. With regard to the other two terms, we have from (27)

$$\delta_{\omega, \alpha} W / \delta_{\omega^2} W = -2\pi\alpha N / \omega f_1(n)(n+n_1)^5, \quad \dots \quad (28)$$

and on substituting the values for ω , α , and N for hydrogen ($E=e$), viz.

$$\omega/2\pi = 1.406 \times 10^6 \text{ H}, \quad \dots \quad \dots \quad \dots \quad (29)$$

$$\alpha = 5.5 \times 10^{-5}, \quad \dots \quad \dots \quad \dots \quad \dots \quad (30)$$

$$N = 3.290 \times 10^{15}, \quad \dots \quad \dots \quad \dots \quad \dots \quad (31)$$

we have, since $f_1(n) (=) 1$,

$$\delta_{\omega, \alpha} W / \delta_{\omega^2} W (=) 10^5 / H(n_1 + n)^5, \quad \dots \quad \dots \quad (32)$$

where $(=)$ stands for equality of order of magnitude only.

Now the smallest value for H which will give a measurable second-order effect is of the order 10^6 Gauss; so that we have for a measurable effect :

$$|\delta_{\omega, \alpha} W / \delta_{\omega^2} W| < 1/10(n_1 + n)^5.$$

Thus for the Balmer Series ($n_1 + n = 2$) the ratio is less than 10^{-2} , and it is still less for the enhanced series ($n_1 + n > 2$). It must, nevertheless, be noted that for fields higher than $H(=)10^8$ Gauss, although the above ratio is reduced to less than 10^{-4} , yet the $\delta_{\omega, \alpha} W$ term would lead to measurable effects. Such very high fields are, however, not likely to be attained at present. We thus see that the only second-order term that has any importance in (27) is the term in ω^2 , and the effect of the field may therefore still be described as a splitting of each of the fine structural components into a Zeeman multiplet. This multiplet is no longer a simple triplet, however, but may be described as a splitting of each of the components of the simple Zeeman triplet into a number of "sub-components." The number of these sub-components depends on $(n_1 + n)$, i. e. on the value of the constant series term of the spectral "line" in question. Thus there are $(n + n_1 + 1)$ sub-components of the middle member of the triplet ($m_3 - n_3 = 0$), $(n + n_1 + 1)$ of the "violet" member ($m_3 - n_3 = +1$), and

$(n+n_1)$ of the "red" member ($m_3-n_3=-1$), altogether $3(n+n_1)+2$ sub-components. One of these, belonging to the middle member of the triplet and corresponding to $m_3=n_3=0$, always occupies the position of the original line. It is also to be noted that, as in the case of the Stark effect*, this second-order deviation from symmetry increases as we approach the more violet end of a given series, *i. e.* as m_1+m increases. This is on account of the occurrence of $(m_1+m)^3$ in the expression for $\delta\nu$ [see equations (33) and (34) below]. Thus for the Balmer Series the effect would be more pronounced for H_β than for H_α , and so on.

§ 4. Application to the Balmer Series.

We choose H_γ as an example. We have from (27), on restricting ourselves to the second-order effect and dropping the suffix ω^2 for brevity,

$$\delta\nu = \omega^2(Z_m - Z_n)/2N \cdot (2\pi)^2, \dots \quad (33)$$

where

$$\left. \begin{aligned} Z_m &= (m_1+m)^3 m_3 [1 + 3m_3/2(m_1+m)], \\ Z_n &= (n_1+n)^3 n_3 [1 + 3n_3/2(n_1+n)]. \end{aligned} \right\} \dots \quad (34)$$

For H_γ , since $m_1+m=5$, $n_1+n=2$, (34) reduces to

$$\left. \begin{aligned} Z_m &= 125m_3(1+3m_3/10), \\ Z_n &= 8n_3(1+3n_3/4). \end{aligned} \right\} \dots \quad (34a)$$

And from (33) we have for the increment of wave-length $\delta\lambda$

$$\delta\lambda = -\lambda^2 \omega^2 [Z_m - Z_n]/2Nc \cdot (2\pi)^2. \dots \quad (35)$$

On putting $\lambda=434 \times 10^{-4}$ and substituting for N and ω from (31) and (29) respectively for a hypothetical magnetic field :

$$H = 10^6 \text{ Gauss}, \dots \quad (36)$$

we have

$$\delta\lambda' = -1.89 \times 10^{-8} [Z_m - Z_n], \dots \quad (37)$$

where $\delta\lambda' = \delta\lambda \times 10^8$, *i. e.* where $\delta\lambda'$ is measured in Angström units.

The different possible values of Z_m and Z_n are given in Table A, and the values of $(Z_m - Z_n)$ corresponding to the three components of the simple Zeeman triplet are given in Table B, together with the values of $\delta\lambda'$ calculated from (37). Table B has been arranged so that the respective positions

* See A. M. Mosharrafah, Phil. Mag. vol. xlix. p. 373 (August 1922).

TABLE A.

	a.	b.	c.	d.	e.	f.	$n_s =$	I.	II.	III.
$m_3 =$	5	4	3	2	1	0				
$Z_m =$	1562·5	1100	712·5	400	162·5	0	$Z_n =$	2	1	0

TABLE B.

"Violet" Component, $m_3 - n_3 = +1.$			Middle Component, $m_3 - n_3 = 0.$			"Red" Component, $m_3 - n_3 = -1.$			
I. c.	II. d.	III. e.	I. d.	II. e.	III. f.	I. e.	II. f.		
$Z_m - Z_n \dots\dots\dots$	672·5	386	162·5	360	148·5	0	122·5	-14	
$\delta\lambda' \dots\dots\dots$	-1·27	-73	-31	-68	-28	0	-23	+03	

of the sub-components are, in each of the three cases, the same as they would appear on a photographic plate with the usual convention. We note that all displacements are towards the violet, except in the case of one of the sub-components of the red component, which is very slightly displaced towards the red. The greatest value of $(-\delta\lambda)$ occurs for the violet component, and the least value for the red component: and this applies to all members of the Balmer series.

Summary.

- (1) A second approximation to the theory of the simple Zeeman effect is worked out, based on the extended form of the quantum restrictions already adopted in a previous paper.
- (2) It is shown that the method of separation of the variables can be successfully applied for higher approximations than the first to a hypothetical motion which possesses the same energy as the actual motion.
- (3) The analysis takes account of the refinement of Relativity, but it is shown that the second-order effect of this refinement is negligible compared with that of the field.
- (4) The theory predicts a modification in the simple Zeeman triplet, which may be described as a splitting of each of its three components into a number of "sub-components." The general character of these sub-components is discussed.
- (5) The results are worked out fully in the case of H_γ for a hypothetical field of 10⁶ Gauss, where second-order displacements ranging from +·03 Å. to -1·27 Å. are predicted.

APPENDIX (to § 2).

To find $\int_0^{T_\psi} \sqrt{(1-\beta^2)} dt$ for the Bohr-Sommerfeld atom, where T_ψ is the time from $\psi=0$ to $\psi=2\pi$:

Let (r, ϕ) be polar coordinates in the plane of motion of the electron, so that

$$\tan \phi = \tan \psi \cos \alpha, \dots \quad (i.)$$

where α is the angle between the planes of ψ and ϕ , and the initial lines $\phi=0, \psi=0$ are both perpendicular to the line of intersection of these two planes. We see from (i.) that as ψ changes from 0 to 2π , ϕ changes

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from 0 to 2π also, so that we have

$$T_\psi = T_\phi, \dots \quad (\text{ii.})$$

where T_ϕ is the period for ϕ . Let T_r be the time from $r=\text{minimum}$ to $r=\text{maximum}$ and back again. We have by a well-known result to the first order in $1/c^2$:

$$T_\phi = T_r(1 - e^2 E^2 / 2p_0^2 c^2), \dots \quad (\text{iii.})$$

or since

$$p_0 = nh/2\pi, \dots \quad (\text{iv.})$$

we have from (ii.), (iii.), and (iv.)

$$T_\psi = T_r(1 - \alpha/2n^2), \dots \quad (\text{v.})$$

where α is defined by equation (15) of the text. Thus to the first order in α

$$\int_0^{T_\psi} \sqrt{(1 - \beta^2)} dt = (1 - \alpha/2n^2) \int_0^{T_r} \sqrt{(1 - \beta^2)} dt. \quad (\text{vi.})$$

Now we see from (7 α) and (12) of the text that

$$\sqrt{(1 - \beta^2)} dt = m_0 dr / \sqrt{(A + 2B/r + C/r^2)};$$

so that

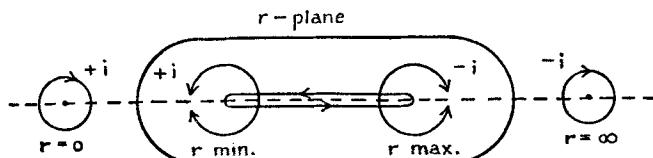
$$\int_0^{T_r} \sqrt{(1 - \beta^2)} dt = -m_0 J_r, \dots \quad (\text{vii.})$$

where

$$J_r = \int_0^r dr / \sqrt{(A + 2B/r + C/r^2)} \dots \quad (\text{viii.})$$

and the negative sign is introduced on account of the negative nature of the integrand. J_r may now be evaluated by the usual method of contour integration in the complex plane. We have to find the residues of the integrand at $r=0$ and $r=\infty$. At $r=0$ it behaves as

$$\frac{1}{\sqrt{C}} \int_0^r r dr (1 + Ar^2 + 2Br)^{-1/2},$$



which is regular. So that putting $r=1/s$, we have

$$\left. \begin{aligned} J_r &= -\frac{1}{\sqrt{A}} \int_0^r (1 - Bs/A + \dots) ds/s^2 \\ &= -2\pi i \times B/A \sqrt{A}, \end{aligned} \right\}, \quad (\text{ix.})$$

where it is observed that the sense of rotation at $r=\infty$ is

negative. Also since $(-1/\sqrt{A})$ is seen from (ix.) to govern the sign of the integrand at $r=\infty$ it follows (see figure) that $(-1/\sqrt{A})$ must be negative and imaginary, and therefore \sqrt{A} must be taken as the negative (imaginary) root of A. On substituting for A and B in (ix.) from (8) of the text we have

$$J_r = -2\pi ieEm_0 [2m_0W]^{-3/2} [1 + W/4m_0c^2 + \dots],$$

which yields to the first order on substituting for W from (25),

$$J_r = -(n_1 + n)^3 h^3 [1 - \alpha \{\frac{1}{4} + 3\phi_1(n_1/n)\}/2(n_1 + n)^2]/(2\pi eEm_0)^2, \quad . . . \quad (x.)$$

and from (vi.), (vii.), and (x.) we have

$$\int_0^{T_\psi} \sqrt{(1-\beta^2)} dt = T_0 [1 - \alpha f_2(n)], \quad . . . \quad (xi.)$$

where T_0 has the same meaning as in the text and

$$\begin{aligned} f_2(n) &= \{\frac{1}{4} + 3\phi_1(n_1/n) + (1+n_1/n)^2\}/2(n_1 + n)^2 \\ &= [1 + 5n_1/2n + n_1^2/2n^2]/(n_1 + n)^2 \text{ from (26 \(\alpha\))}. \end{aligned}$$

This is the result quoted in the text.

January 1923.

LVI. Electrical Discharges in Geissler Tubes with Hot Cathodes. By W. H. McCURDY, M.A., 1851 Exhibition Scholar, Princeton University*.

IN a recent number of the 'Physical Review,' Duffendack † reported results obtained from work on low-voltage arcs, stimulated by the emission from a hot cathode, in diatomic gases. As his work dealt only with the arc characteristics, it was thought possible that additional light might be thrown on the process of ionization by a study of the discharge in Geissler tubes, if a hot filament were used as cathode to stimulate the discharge. This eliminated the uncertainty as to the source of the electrons which produced the ionization in the tube, and, at the same time, overcame the very high cathode fall of potential encountered in cold electrode tubes. With an apparatus provided with a hot cathode and a movable anode, it should be possible to study the successive stages in

* Communicated by Professor K. T. Compton.

† Phys. Rev. vol. xx. No. 6, p. 665.